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Critical Assessment of Optical Properties of CVD Diamond Films

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Abstract

The basic phenomena that determine the optical properties of diamond, which include the electronic band structure, the phonon structure, and defects, are discussed. Experiments on chemical vapor deposited diamond relevant to its applications as an optical material are reviewed. The most immediate application is the diamond x-ray window. Other applications, such as infrared transmissive elements and coatings, will require considerable improvement in material quality. Surface roughness is a major impediment. The ability to deposit smooth surfaces would make diamond considerably more attractive as optical material. Diamond also has promise as a blue luminescent or laser material. Identifying and controlling the relevant luminescent centers will be needed to improve the quantum efficiencies of such devices.

1. INTRODUCTION

Diamond has a combination of excellent properties that make it a desirable material for many optical applications: optical transparency from the ultraviolet to the far infrared, the greatest hardness and highest room temperature thermal conductivity of any material, and great chemical inertness. The high cost and limited dimensions of optical quality diamond have limited its use to a few specialized optical applications; the best optical quality diamond still comes from natural sources. However, new chemical vapor deposition (CVD) methods offer the promise of diamond films or plates in large sizes, making possible the wide use of diamond optical coatings and bulk optics [1]. The purpose of this review is to evaluate the properties of CVD diamond for optical applications.

2. FUNDAMENTAL OPTICAL PROPERTIES OF DIAMOND

The crystal structure of a material determines many of its properties. The diamond crystal structure consists of two interpenetrating face-centered cubic lattices of carbon atoms. Each carbon atom is surrounded by four other carbon atoms in a regular tetrahedral configuration and the bonding between the atoms is sp^3 bonding. The lattice constant, equal to the length of an edge of the cubic unit cell, is 0.3567 nm and the C-C bond length is 0.1545 nm at 298 K. The short bond length and high strength of the C-C bond accounts for the great hardness of diamond and its large elastic moduli.

An optical material is transparent to light of a particular wavelength

when the energy of a quantum of light, the photon, falls between the lattice vibration energies in the infrared and the energies of interband electronic transitions at or above the electronic energy gap, E_g . The material absorbs light when an infrared photon creates a phonon or when a high-energy photon excites an electron from a filled band to an unfilled band. E_g arises from the electronic band structure of an insulating crystal. The band structure represents the allowed energies of an electron as a function of momentum. E_g is the minimum energy required to excite an electron from a filled valence band to an empty conduction band. Figure 1 shows a calculated band structure for diamond [2]. In diamond, $E_g=5.45$ eV, corresponding to a wavelength $\lambda=227$ nm, and the gap is indirect, meaning that an electron has a different momentum at the bottom of the conduction band than at the top of the valence band. Because the photon momentum is very small, a phonon must be absorbed or emitted for an indirect transition to occur. Direct transitions can occur above a higher energy gap; for diamond, the direct gap is 7.2 eV.

The phonon spectrum gives the allowed energies for quanta of lattice vibrations, the phonons, as a function of momentum. The diamond phonon spectrum, shown in figure 2 [3], consists of two sets of curves, the lower-energy acoustic branches and higher-energy optic branches. In most materials, infrared absorption occurs when a photon creates one optic phonon. However, in pure diamond, the symmetry of the crystal lattice does not permit the absorption of one photon to create one optic phonon. Higher-order processes, in which the absorption of one photon creates two or three phonons, are responsible for the infrared absorption of pure diamond between 2.5 to 7 μm .

Photons with energy much greater than the energy of a single phonon can scatter from the crystal by creating a phonon. When the phonon is from the optic branch, this process is called Raman scattering. Raman spectroscopy is one of the major diagnostic tools used to evaluate the quality of CVD diamond.

The optical properties of diamond are strongly affected by defects. First are lattice defects including dislocations, stacking faults, twin boundaries, and grain boundaries. It is not known how these defects affect the optical transmission, although dislocations have been associated with luminescence. Next are point defects, impurities, and defect complexes. Single-atom impurities that occur in diamond include nitrogen, boron, silicon, and hydrogen. Defects and impurities may cause optical absorption in several ways. First, they may break the lattice symmetry, causing one-phonon infrared absorption, which is forbidden in pure diamond. Second, transitions between the localized electronic or vibrational states of a defect may cause absorption lines or bands that are specific to the defect.

Atomic nitrogen, boron, and hydrogen are known to cause additional absorption in diamond [4,5]. Nitrogen introduces electronic absorption below E_g in the ultraviolet and blue regions of the spectrum, causing a yellow coloration for diamond doped with single nitrogen atoms. It also increases the infrared absorption beyond 10 μm . Boron gives rise to electronic absorption that peaks in the near-infrared at approximately 2.5 μm . The tail of the boron absorption spectrum extends to approximately 0.5 μm in the visible region, causing a blue coloration for boron-doped diamond. Hydrogen rich diamonds show significant absorption in the visible and from 400 to 4900 cm^{-1} in the infrared [5]. The latter absorption is attributed to stretching and bending of C-H bonds, and, in nitrogen and hydrogen rich diamonds, to N-H bonds.

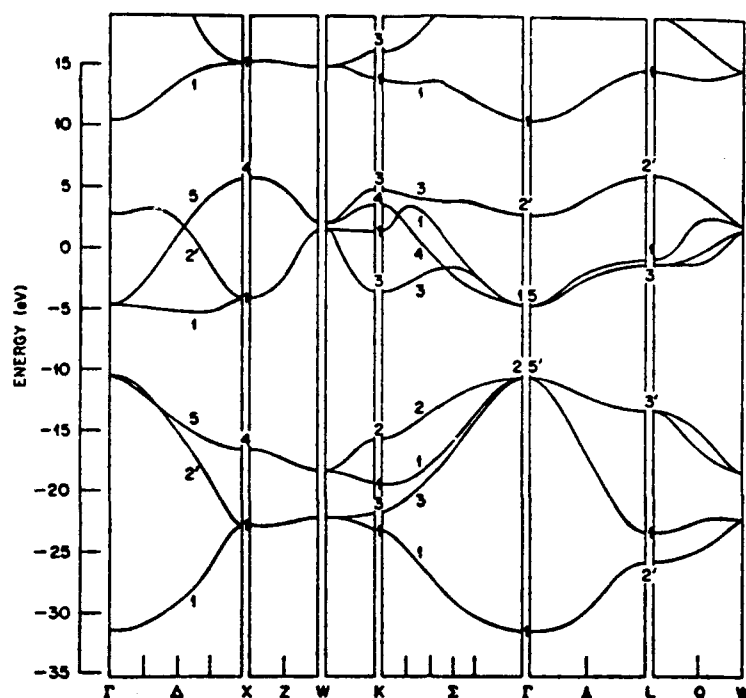


Figure 1. Band structure of diamond.

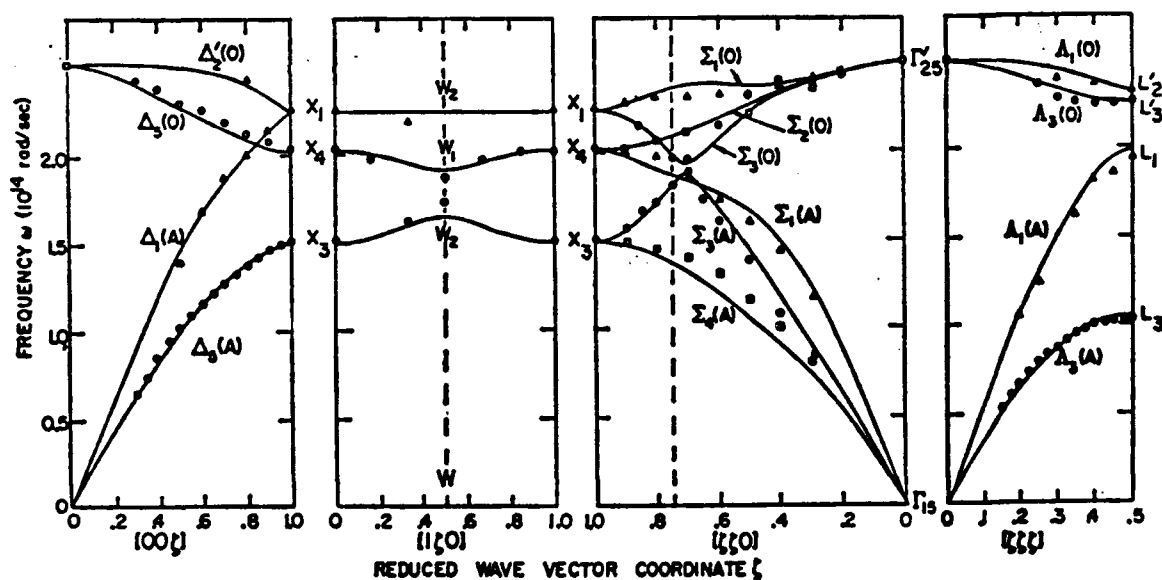


Figure 2. Phonon spectrum of diamond.

Defects in diamond give rise to optical emission when excited by high energy electrons (~1 to 50 keV) or by photons of energies higher than E_g [6]. Luminescence from defects is the basis for the diamond laser [7] and for diamond electroluminescent devices [8].

A key optical property of diamond is its refractive index, n . Table 1 lists n of bulk crystalline diamond at selected wavelengths [9].

Table 1
Refractive Index n of Diamond at Selected Wavelengths

Wavelength μm	n	Wavelength μm	n	Wavelength μm	n
0.250	2.6333	0.700	2.4062	9.00	2.3758
0.300	2.5407	0.750	2.4028	10.00	2.3756
0.350	2.4928	2.50	2.3786	12.00	2.3755
0.400	2.4641	3.00	2.3782	14.00	2.3753
0.450	2.4454	4.00	2.3773	16.00	2.3752
0.500	2.4324	5.00	2.3767	18.00	2.3751
0.550	2.4230	6.00	2.3763	20.00	2.3750
0.600	2.4159	7.00	2.3761	25.00	2.3749
0.650	2.4105	8.00	2.3759		

3. OPTICAL TRANSMISSION OF CVD DIAMOND

High optical transmission is a key property of diamond for applications such as optical films, windows, and infrared domes. Transmittance spectra for bulk diamonds have been obtained by several authors [4,10] but will not be shown here for brevity.

Several researchers have examined the transmissive properties of CVD diamond films [11-17]. The general conclusion to be drawn from this work is that the specular transmittance of as-grown CVD diamond films is limited by the surface roughness of the growth surface. The smoother the surface, the shorter is the wavelength at which significant transmittance can occur.

Several authors have obtained satisfactory fits to their transmittance spectra by employing models that take into account the surface roughness [11,13]. In the far infrared, where the wavelength of the radiation was significantly greater than the surface roughness of their films, Bi et al. [11] were able to fit their transmittance spectra to the transmittance of a transparent plate in air. At shorter wavelengths, optical scattering from the rough surfaces acts to decrease the specular transmittance. The transmittance, τ , was fit to the expression

$$\tau = \frac{(1-R_0)^2 \exp(-a/\lambda^2)}{1+R_0^2 \exp(-b/\lambda^2) - 2R_0 \cos(4\pi nd/\lambda) \exp[-b/(2\lambda^2)]} \quad (1)$$

where λ is the wavelength, a and b are adjustable parameters that account for scattering by the rough surfaces [18], and R_0 is the reflectivity of a smooth surface. The best fit was obtained with $a=2.3 \mu\text{m}^2$, $b=350 \mu\text{m}^2$, $d=8.6 \mu\text{m}$, and $n=2.4$. Nearly all of the observed attenuation can be accounted for by optical scatter from the rough surfaces. A spectral absorption feature observed near 2800 cm^{-1} was attributed to an infrared active C-H stretching mode. This feature has been observed by other workers.

Gatesman et al. [13] have examined the far infrared transmittance of thick CVD diamond films and have derived a model for the complex refractive index, $n-ik$. Measurements were conducted over the range $25\text{-}350 \text{ cm}^{-1}$ on freestanding films grown by microwave plasma CVD. The attenuation of the transmittance was attributed both to surface roughness and to free carrier

absorption. A model similar to that of Bi et al. was used to model the wavelength dependence of the surface scatter. However, Gatesman et al. found that surface roughness alone could not account for all of the attenuation. This additional attenuation, which was especially strong in their thickest specimen, was attributed to free carrier absorption, probably due to graphitic material mixed with the diamond. The expression for the complex refractive index in the presence of free carrier absorption is

$$(n-ik)^2 = n_0^2 \left[1 - \frac{\omega_p^2}{\omega(\omega+i\gamma)} \right], \quad (2)$$

where, ω_p is the plasma frequency defined by $\omega_p^2 = 4\pi N e^2 / (m n_0^2)$, n_0 is the refractive index of the material in the absence of free carriers, N is the density of free carriers, e is the electronic charge, m is the free carrier mass, ω is the frequency of the radiation, γ is a damping factor, and $i = \sqrt{-1}$. If we assume $\omega \gg \gamma$, then $k = n_0^2 \omega_p^2 \gamma / (2n\omega^3)$. This implies that k should be proportional to λ^3 for free carrier absorption. However, the best fit occurred when k was proportional to λ^2 , which is within the range of reported values for free carrier absorption in other materials. The best fit to the transmittance data was obtained with $n=2.36$, $k=15\lambda^2$, where λ is in cm, and $\sigma=2.1 \mu\text{m}$ where σ is the root mean squared surface roughness. The value of n is slightly lower than that reported by Edwards and Ochoa for bulk diamond. Figure 3 shows the observed transmittance spectrum and the numerical fit.

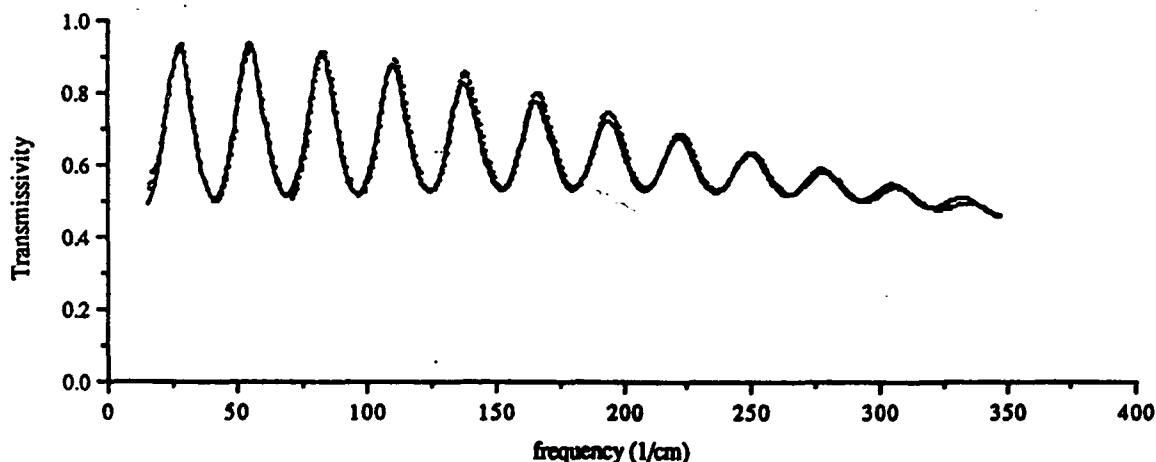


Figure 3. FTIR transmissivity of CVD diamond and model fit [13].

4. OPTICAL EMISSION

Diamond emits optical radiation when subject to electric currents (electroluminescence) [19], photon beams (photoluminescence) [20,21] and electron beams (cathodoluminescence) [20,21]. The emission spectra from these different sources can be similar or different. Figure 4 is an example of a cathodoluminescence spectrum of CVD diamond [22]. The principal spectral features are attributed to defects which were previously observed

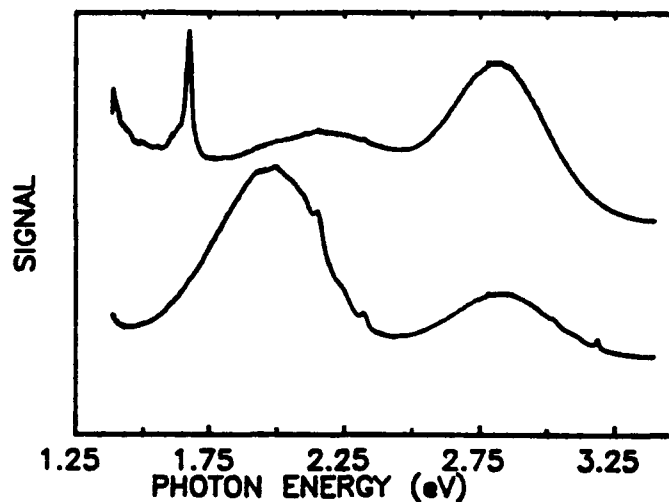


Figure 4. Cathodoluminescence emission spectra from CVD diamond films [22].

in natural diamond. These include a zero-phonon line at 1.68 eV, which is now believed to be due to a silicon impurity; a zero phonon line at 2.156 eV, with an associated vibronic band centered near 2 eV, due to a nitrogen-vacancy (N-V) complex; another zero-phonon line at 2.326 eV due to a different N-V complex; a broad violet band centered at 2.85 eV, due to a dislocation related defect; and a zero-phonon line at 3.188 eV due to an interstitial nitrogen atom or a nitrogen-carbon complex.

Taniguchi et al. have constructed a blue electroluminescent device from diamond made by the hot filament CVD method [8]. The device was made of diamond sandwiched between insulating layers of HfO_2 and Al_2O_3 . N-type Si was used as the substrate and base electrode. Indium tin oxide, an optically transparent electrical conductor, was used as the top electrode. A blue emission band with a peak centered between 430 and 440 nm (2.82-2.88 eV) was observed from almost all devices constructed. The origin of the emission is not certain; however, the spectrum is similar to the electroluminescence spectra observed by Prior and Champion [19] in natural bulk diamond, and to the broad violet cathodoluminescence band observed in CVD diamond [22]. The maximum luminance was too low for practical use; however, further work may improve device performance.

5. X-RAY WINDOW

Because of its low atomic number, carbon is highly transparent to x-ray radiation. The excellent mechanical properties of diamond make it useful as an ultrathin x-ray window for an energy dispersive x-ray fluorescence detector [23]. This is the first optical application of CVD diamond. In this application diamond is replacing beryllium which must be made considerably thicker to support vacuum. The properties of diamond also make this material an excellent candidate as a membrane support for x-ray lithography of integrated circuits [24].

6. CONCLUSIONS

The superior properties of diamond make it a candidate for a number of optical applications. The most immediate application is the diamond x-ray window. However, other applications, such as infrared transmissive elements and coatings, will require considerable improvement in the quality of the material. Surface roughness is a major impediment. The ability to deposit smooth surfaces would make diamond considerably more attractive as an optical material. Polishing is being pursued as a means for making smooth CVD diamond surfaces [15,25,26]. Diamond also has promise as a blue luminescent or laser material. Identifying and controlling the relevant luminescent defect centers will be needed to improve the quantum efficiencies of such devices.

7. ACKNOWLEDGEMENT

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8. REFERENCES

- 1 V.P. Varnin, B.V. Deryagin, D.V. Fedoseev, I.G. Teremetskaya, and A.N. Khodan, *Sov. Phys. Crystallogr.* 22, 513-515 (1977); S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, *Jpn. J. Appl. Phys.* 21, L183 (1982).
- 2 G.S. Painter, D.E. Ellis, and A.R. Lubinsky, *Phys. Rev. B* 4, 3610-3622 (1971).
- 3 J.L. Warren, J.L. Yarnell, G. Dolling, and R.A. Cowley, *Phys. Rev.* 158, 805-808 (1967).
- 4 S. Musikan, Optical Materials (Marcel Dekker, New York and Basel, 1985) pp. 113-115.
- 5 E. Fritsch and D.V.G. Scarratt, *SPIE Vol. 1146 - Diamond Optics II*, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1989) pp. 210-206.
- 6 C.D. Clark, R.W. Ditchburn, and H.B. Dyer, *Proc. R. Soc. A* 234, 363-381 (1956); C.D. Clark, R.W. Ditchburn, and H.B. Dyer, *Proc. R. Soc. A* 237, 75-89 (1956).
- 7 S.C. Rand and L.G. DeShaser, *Opt. Lett.* 10, 481-483 (1985).
- 8 Y. Taniguchi, K. Hirabayashi, K. Ikoma, N. Iwasaki, K. Kurihara, and M. Matsushima, *Jpn. J. Appl. Phys.* 28, L1848-1850 (1989).
- 9 F. Peter, *Z. Physik* 15, 358-368 (1923); S. von Rösche, *Opt. Acta* 12, 253-260 (1965); D.F. Edwards and E. Ochoa, *J. Opt. Soc. Amer.* 71, 607-608 (1981); D.F. Edwards and H.R. Philipp in Handbook of Optical Constants of Solids, E.D. Palik, editor (Academic Press, Orlando, 1985) pp. 665-673.
- 10 M. Seal and W.J.P. van Enckevort, in *SPIE Vol. 969 - Diamond Optics II*, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1988) pp. 144-152.
- 11 X.X. Bi, P.C. Eklund, J.G. Zhang, A.M. Rao, T.A. Perry, and C.P. Beetz, Jr., *J. Mater. Res.* 5, 811-817, 1990; X.X. Bi, P.C. Eklund, J.G. Zhang, A.M. Rao, T.A. Perry, and C.P. Beetz, Jr., in *SPIE Vol. 1146 - Diamond Optics II*, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1990) pp. 192-200.
- 12 X.H. Wang, L. Pilione, W. Zhu, W. Yarbrough, W. Drawl, and R. Messier,

- in SPIE Vol. 1325 - Diamond Optics III, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1990) pp. 160-167.
- 13 A.J. Gateman, R.H. Giles, J. Waldman, L.P. Bourget, and R. Post, in SPIE Vol. 1325 - Diamond Optics III, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1990) pp. 170-177.
 - 14 Y. Cong, R.W. Collins, G.F. Epps, and H. Windischmann, Appl. Phys. Lett. 58, 819-821 (1991).
 - 15 K.A. Snail, L.M. Hanssen, A.A. Morrish, and W.A. Carrington, in SPIE Vol. 1146 - Diamond Optics II, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1989) pp. 144-151.
 - 16 T. Feng, in SPIE Vol. 1146 - Diamond Optics II, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1989) pp. 159-165.
 - 17 C.E. Johnson and W.A. Weimer, "Optical properties of microwave-plasma-assisted-CVD diamond film," in SPIE Vol. 1146 - Diamond Optics II, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1989) pp. 188-191.
 - 18 H.E. Bennett and J.M. Bennett, in Physics of Thin Films, Vol. 4, edited by G. Hass and R.E. Thun (Academic Press, New York and London, 1967), p. 1.
 - 19 J.R. Prior and F.C. Champion, Proc. Phys. Soc. 80, 849-859 (1962).
 - 20 G. Davies, in Chemistry and Physics of Carbon, Vol. 13, ed. by P.L. Walker and P.A. Thrower (Marcel Dekker, 1977), p. 1.
 - 21 J. Walker, Rep. Prog. Phys. 42, 1605-1659 (1979)
 - 22 L.H. Robins, L.P. Cook, E.N. Farabaugh, and A. Feldman, Phys. Rev. B 39, 13367-13377 (1989).
 - 23 M.G. Peters, J.L. Knowles, M. Breen, and J. McCarthy, in SPIE Vol. 969 - Diamond Optics II, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1988) pp. 217-224.
 - 24 H. Windischmann and G.F. Epps, J. Appl. Phys. 68, 5665-5673 (1990)
 - 25 M. Yoshikawa, in SPIE Vol. 1325 - Diamond Optics III, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1990) pp. 210-221.
 - 26 A.B. Harker, J. Flintoff, and J.F. DeNatale, in SPIE Vol. 1325 - Diamond Optics III, edited by A. Feldman and S. Holly (SPIE, Bellingham, Washington, 1990) pp. 222-229.